Lithium vanadate, Li₃VO₄ is isostructural to Li₃PO₄ – an advanced material for rechargeable lithium-ion batteries. Li₃VO₄ and Li₃PO₄ are known to have several polymorphs: the βᵢᵢ-forms (sp. gr. Pmn₂₁) are stable in low temperature and the γ-forms (sp. gr. Pmnb) are generally stable in high temperature. Lithium vanadate shows high conductivity in the γ-form because of the lithium-ion mobility in the structure [1]; relatively high room temperature conductivity is reported for the βᵢᵢ-form [2]. Furthermore, the βᵢᵢ-form has attractive properties for optic materials: it was found that βᵢᵢ-Li₃VO₄ shows second harmonic generation activity [3]. The crystal structures of both polymorphs are built up of oxygen atoms in the hexagonal close packing oriented perpendicular to the c axes. The Li⁺ and V⁵⁺/P⁵⁺ cations occupy half of the tetrahedral voids. The non-centrosymmetric βᵢᵢ-form consists of only corner-sharing tetrahedra. The γ-form is built up by both corner and edge sharing tetrahedra. In the Li₃PO₄ structure a/c unit cell parameters of the two different polymorphs are almost the same – 6.115(1)/4.8554(1) and 6.120(2)/4.9266(7) Å, for βᵢᵢ- and γ-form, respectively; whereas the b parameter of βᵢᵢ-form, 5.2394(11) Å, is doubled in the γ-form and [4][6][4] equal to 10.490(3) Å. Numerous synthetic compounds with the general formula [⁴]Li₁ᵦ[⁶]M[⁴]TO₄ (M = Fe, Mn, Co, Ni, Zn; T = P, V, As, Si, Ge) are closely related to Li₃PO₄. Such compounds show similar physical properties and form solid solutions between the end members. Moreover, γ-Li₃PO₄ occurs in nature as the mineral lithiophosphate; its Na-species is known as the mineral nalipoite.

NaLi₂PO₄.

Translucent pale yellow crystals of Li₃(V,P)O₄ with prismatic shape were formed by hydrothermal synthesis. A mixture of Li₃PO₄, Li₂CO₃, V₂O₅, and H₂O in a weight ratio of 1 : 1 : 1 : 5 was placed in a 4 ml PTFE-lined stainless steel autoclave. The reaction time at T = 280°C and P = 70 bar was 18 days. The presence of V, P, and O in the samples was confirmed by qualitative X-ray elemental microanalysis.

The Li₃(V₀.₇P₀.₃)O₄ crystal structure was determined by single crystal X-ray diffraction: a = 6.3050(12), b = 10.921(2), c = 4.9450(10) Å, Pbn₂₁, Z = 4, ρ = 2.799 g/cm³, R₁ = 0.0279, ωR₂ = 0.0432. The crystal chemical similarity of the discussed compounds allow us to consider the Li₃(V,P)O₄ as a perspective material for electrochemical applications. Note that in the [⁴]Li₁ᵦ[⁶]M[⁴]TO₄-family, Pbn₂₁ space group is known only for the Li₂CoSiO₄, which also crystallizes in Pmn₂₁, and Pmnb space groups [4].


Keywords: electrochemical materials; lithium vanadate; lithium phosphate